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Issues On The Production And Electrochemical Separation Of Oxygen
From Carbon Dioxide

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ABSTRACT

There is considerable interest at the present time in in-situ propellant manufacturing on the Moon and Mars. One of the concepts of oxygen production that is being actively pursued is the processing of atmospheric carbon dioxide on Mars to produce oxygen by means of thermal decomposition and electrochemical separation. The key component of such a production facility is the electrochemical separation cell that filters out the oxygen from the gas mixture of carbon dioxide, carbon monoxide and oxygen. Efficient design of the separation cell and the selection of electrolyte and electrode materials of superior performance for the cell would translate to significant reduction in the power requirement and the mass of the production facility. The objective of this investigation is to develop the technology required to produce the cells in-house and test various electrolyte and electrode materials systematically until the optimal combination is found. The effect of fabrication methods on the performance of the cell will be studied. Tests will be conducted to investigate the performance of the cell at sub atmospheric (< 1 bar) CO₂ supply pressures. An effective technique has been developed for the fabrication of disk shaped cells. Zirconia and Ceria cells have been made in-house. Complete modules of the electrochemical cell and housings have been designed, fabricated and tested. Extensive experiments aimed at characterizing the materials will be underway shortly.

INTRODUCTION

With the renewed interest in space exploration, and in light of the The Report of the National Commission on Space [1], it is expected that some sort of mission, either manned or unmanned, will be forthcoming for surface exploration or sample return from Mars. It has been recognized that one way to reduce the overall weight requirements of such a mission, and hence its costs, is the use of in-situ propellant manufacturing [2]. To this end, several concepts have been proposed for the manufacturing of oxygen from local Martian resources [3-5]. The production of oxygen alone

would provide a tremendous advantage for sample return missions, in which oxygen is the primary propellant mass. The Martian atmosphere, with its known composition of 95.3% carbon dioxide, can provide an excellent source of oxygen. Since such a production plant would be independent of landing site, it is ideally suited for such a concept.

Although the design of a complete oxygen production plant involves many different components, such as collection, separation, storage, and associated power systems, the main consideration here is the oxygen separation system. Carbon dioxide is thermally decomposed into carbon monoxide and oxygen by heating it to high temperatures. Oxygen is separated from the gas mixture using an electrochemical separation cell. With the design of the most efficient system possible, savings can be realized on the power requirements and weight characteristics of the overall plant.

The basic separation cell is shown schematically in Fig. 1. The oxygen separation capability of the system is due to the oxygen ion conduction of the electrolyte material selected. Oxygen vacancies exist in the crystal lattice of the electrolyte. These vacancies provide conduction sites for the transport of oxygen ions through the electrolyte. The driving force for the ions is a potential applied across the electrolyte material. CO_2 is heated so that it thermally dissociates into CO and O_2 . The gas mixture is then passed over the cell which consists of an electrolyte sandwiched between electronically conductive porous electrodes. The diatomic oxygen diffuses through the porous electrode to the electrolyte/electrode interface, and the O_2 molecule decomposes into oxygen ions with a negative charge of two. The applied potential supplies the electrons at the cathode, and provides the potential gradient to drive the oxygen ions through the crystal lattice structure. The oxygen ions move from vacancy to vacancy until they arrive at the electrolyte/electrode anode interface. Here they give up the excess electrons and reform O_2 , which then diffuses through the porous electrode. The pure diatomic oxygen can then be collected for use.

The properties of the electrolyte and the electrode are of paramount importance in determining the overall characteristics of the cell. For example, operation at a high temperature is desirable since this improves the oxygen ion conductivity through the lattice. Also, a porous electrode is preferred since the oxygen must be able to pass freely through it, however good electronic conductivity (which requires less porosity) is also necessary. These, and other requirements, along with the restrictions they impose on material selection, are considered in more detail in the following sections.

In order to be able to examine many different types of electrolyte/electrode combinations, an

experimental system was devised which allows for easy investigation of manufactured cells. The disk design was selected because of its simplicity. Once the electrolyte has been manufactured, the electrode is applied and the system is sealed inside a manifold. The process is described in more detail in a later section. With this design, the fabrication of cells is quick and relatively easy, allowing for experimentation with many different combinations of materials.

The main emphasis at this time has been in developing an understanding of the electrochemical processes, and in the fabrication techniques associated with building an operational cell. Once this groundwork has been laid, it will then be possible to select electrolyte/electrode combinations that meet the requirements for an actual system.

THE ELECTROLYTE

The single most important element in the electrolytic separation of oxygen from carbon dioxide is the selection of the electrolyte. A substantial amount of work has been performed in this area by Suitor, et. al. [6], who have identified a search process based on certain criteria. The present work parallels their approach, which identifies classes of likely compounds and then attempts to use a systematic approach in selecting potential oxygen ion conductors. It is desirable to select an electrolyte that has the highest possible conductivity at the lowest possible operating temperature, so as to reduce the overall mass and power requirements of an oxygen plant.

Theory

The most important consideration in selecting an electrolyte is the overall conductivity. It must have the maximum possible oxygen ion conduction with very little electron or secondary ion conduction. It must also be non-porous and have good micro-structural stability. The electrolyte must also be stable in chemistry and in phase during prolonged exposure to high temperatures and repeated cycling. In addition, it must resist cracking due to mechanical stresses that arise due to differing thermal expansion coefficients of the electrode and casing, and it must be economical and relatively easy to fabricate.

To achieve the highest possible oxygen ion conductivity it is required to have a high concentration of oxygen vacancies, low activation energy, and weak bonding at the oxygen sites. Suitor, et. al. [6] identify compounds by fitting them to these three categories. High vacancy concentrations can be found in defect structure oxides, materials doped with lower valence cations, and open structures where oxygen ions occupy interstitial sites. Low activation energies are found in oxides with low packing densities (more open paths are available), and in oxygen salts of large polyvalent single valence cations. Weakly bonded oxygen sites are found in metastable structures and

structures stabilized with large dopant ions, glasses made from oxides of large polyvalent single valence cations, and low packing density oxides with non-equivalent oxygen sites.

An extensive search of currently unknown materials that may meet the above requirements is not feasible, since many of the possible compounds are not researched in the literature [6]. However, known oxygen electrolytes such as Zirconia, Thoria, delta Bismuth Oxide, and Ceria have been extensively investigated by many authors [7-11]. These materials are good oxygen ion conductors and mostly exhibit low electron conductivity. In order to begin the present investigation Zirconia and Ceria were selected because of their availability and ease of fabrication. There is some evidence to indicate that Zirconia may prove to be the most probable choice for an oxygen separation cell [6], even though it does not exhibit the highest conductivity.

Both Zirconia (ZrO_2) and Ceria (CeO_2) are oxides of quadrivalent cations which crystallize with a fluorite, or distorted fluorite, structure (Fig. 2). These oxides become oxygen conductors when they are doped with lower valence cations such as Calcium, Yttrium, or Scandium. These dopants stabilize the cubic fluorite structure and create anion vacancies. The magnitude of the conductivity depends on dopant concentration, type of dopant, and temperature. The effect of dopant concentration for Ytria stabilized Zirconia is shown in Fig. 3 [6]. As the mole percentage of dopant increases, so does the conductivity until it reaches a maximum. This maximum occurs because the migration energy of the oxygen ion increases with the increased presence of dopant cations, even though more oxygen anion vacancies exist. The importance of high conductivity at low temperature is obvious. The savings in power requirements for a cell operating at even 100 °C lower operating temperature is quite significant.

For the present study we investigated only $\text{ZrO}_2\text{-Y}_2\text{O}_3$ 8% mole and $\text{CeO}_2\text{-CaO}$ 15% mole to establish the fabrication techniques required for the electrolyte. These molar percentages represent maximum conductivities based on past investigations [6,12].

Fabrication of the Electrolyte

There are several potential techniques for fabricating the electrolyte that may be used. These include slip casting, tape casting, and cold pressing. Other techniques such as sputtering or flame spraying are not considered because of the difficulty of making uniform, non-porous samples.

Tape casting involves the use of a slurry that is prepared by adding the ceramic powder, solvent, dispersant, and binder and making a smooth paste. The slurry is then poured onto a flat surface, and a blade is drawn over it to cast the slurry into a uniformly thick layer. The net result is a flat, flexible layer of material from which any shape can be cut. This green material can then be

fired to form the electrolyte disk. Cold pressing involves a dry powder consisting of the ceramic powder and binder which is uniaxially pressed to form the disk. The method selected here is the cold pressing because of its simplicity and cost. At this preliminary stage of investigation it is important to be able to produce many disks without much cost and/or involved fabrication techniques. As the investigation progresses it is anticipated that other techniques, such as tape casting, will be considered for the manufacture of the electrolyte disks.

The two electrolytes fabricated at the present time are $\text{ZrO}_2\text{-Y}_2\text{O}_3$ 8% mole and $\text{CeO}_2\text{-CaO}$ 15% mole. The Ceria has been prepared via oxide and nitrate routes. The fabrication techniques for the two electrolytes follow.

In order to prepare the Zirconia disks two commercially available powders were used. These are the TOSOH TZ-8Y and the Magnesium Elektron Inc. SCY8. The method of preparation for the two powders is the same. A 15% volume slurry was made from the dry powder by adding H_2O , and then 1.5% weight binder was added. The mixture was stirred for 20 minutes, and was then pan-dried at 60 °C. The dried powder was then sieved through a #45 sieve to ensure uniform particle size. The fine powder was then ready to be cold pressed into the green disks.

The preparation of the Ceria disks was more involved, since no commercially available Calcia stabilized Ceria was readily available. Two preparation techniques were used to make the powder.

The first technique is preparation via the oxide route. Appropriate quantities of dry Alfa Products CeO_2 (IV) and CaO corresponding to 15% mole are dry mixed and then ball milled in Ethanol (ETOH) for 24 hours. The ETOH is then boiled off by drying at 60 °C, and the powder is calcined at 1000 °C for 12 hours. The calcined powder is then ball milled in ETOH for an additional 12 hours, at which point 0.5% weight organic binder is added. This is then milled for an additional 4 hours. The wet powder is pan-dried at 60 °C and sieved through a #45 sieve for uniformity.

The second technique for preparing the Ceria is via the nitrate route. A 60% volume slurry in water is made from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. This slurry is mixed until a smooth consistency is obtained. While this mixture is being agitated, nitric acid (HNO_3) is added until the solution becomes clear. The CeO_2 powder is then blended into the solution. The H_2O is evaporated by heating over a hot-plate. The recovered powder is then calcined at 1000 °C for 12 hours. The powder is then removed and ball milled in ETOH for 24 hours. A 0.5% weight organic binder is then added to the solution, and the mixture is milled for an additional 2 hours. The final slurry is removed and pan-dried at 60 °C. The powder is then sieved through a #45 sieve for uniformity.

In all cases the binder was added to allow cold pressing of the green disks. A commercially

available Zirconia powder TSAM-105 from Huls America with binder already added was also tried, but was not very successful. It is believed that the particular binder used in this commercial product was not very effective for our application.

Once the finished powders were ready, they were cold pressed in a die. Uniaxial compression of 8000-19000 lbs/in² was used to make the green disks. Several thicknesses ranging from 1-3 mm were produced, with a diameter of 1.5 inches. Once the green disks were formed they were sintered for final use.

The disks were sintered at varying temperatures for different time spans. Because of limited access to a furnace, the disks were sintered at a rapid rate. Typically, the furnace was ramped to 1400 °C in 2 hours, and allowed to remain there for 1/2 hour. The temperature was then ramped to 1600 °C in 1 hour, and remained there for 1 hour. The disks were then removed.

During the cooling of the disks following the firing in the furnace, some of the disks warped. Many disks proved to be unusable because they were not flat. It is believed that the rapid temperature rise caused internal stresses within the disks which caused them to warp. Now, access to a furnace has been obtained with longer usage times, and this problem will be avoided. The placement of flat weights (1 gm/cm²) over the disks during the sintering process has also proven to be helpful in reducing this problem.

At the present time the disks have not been tested for porosity, however they are believed to be quite dense. Analysis of the disks with the aid of an electron microscope for this purpose has been planned for the future.

THE ELECTRODE

The selection of the electrode and the technique used to apply it to the electrolyte surface is very important. The properties of the electrode and the electrolyte/electrode interface are critical to the overall performance of the cell. Typical electrode materials are precious metals and conducting oxides, doped with some impurity, as well as perovskites.

Theory

The most important considerations for the selection of an electrode material are its electronic conductivity, the thermal expansion coefficient, its porosity, oxidation resistance, and chemical and electrical stability. The thermal expansion coefficient must match that of the electrolyte as closely as possible, so that mechanical stresses do not arise at the interface. This could lead to cracking of the electrolyte during prolonged exposure to high temperature and thermal cycling. Also, it is necessary that the electrode be porous so that the oxygen ions can move freely through it. However,

a balance exists between good conductivity and free movement of oxygen ions. Another important consideration in selecting the electrode is the potential catalytic effect that it may have on the oxygen kinetic reactions, both on the cathode and the anode side of the cell [13]. The electrolyte/electrode interface is also of significance. If the electrolyte is very thin, then the major ohmic loss will occur at the interface with the electrode [13]. Minimizing the losses at the point of contact could significantly change the performance of the cell.

Much work has been done with precious metals [14,15] such as Silver, Palladium, and Platinum. They are very expensive and do not match the thermal properties of the electrolyte surface. Other types of electrodes that have been investigated are chemically stable oxides doped with impurities, such as Tin oxide doped Indium oxide [16], and perovskites [6]. These have excellent thermal properties with relation to the electrolytes, and they reduce thermal stresses that may arise during thermal cycling. However, these materials typically have complicated manufacturing and application procedures and hence have not been investigated at the present. At this time we have considered only precious metals. Plans for the future include testing the oxides and perovskites as potential electrodes.

Application of the Electrode

The application of the electrode material to the electrolyte surface can be done in many ways. Direct application techniques include sputtering, vapor deposition, flame spraying, and direct paste application. There is some evidence to suggest that sputtering is not an effective application technique [17], since it can destroy the electrolyte surface. Also, because techniques such as vapor deposition and flame spraying are expensive and difficult, only paste application has been investigated at this time.

The electrode material most often applied to the electrolyte to date is Platinum, although Silver has also been used. Commercially available unfritted Pt paste supplied by Heraeus Cermalloy has been used, and a thin layer of the electrode paste is painted onto the electrolyte surface. The lead wire is a spiraled wire of the same material as the electrode, which is pressed into the paste before it dries. The paste is then set by heating in a furnace to 950 °C. The finished cell, shown in Fig. 4 is then ready to be manifolded.

THE CELL MANIFOLD

Once the electroded disk is made, it is sealed in a manifold for experimentation. The configuration, before being sealed is shown in Fig. 5a, and the schematic of the sealed cell is shown in Fig. 5b. There is a CO₂ supply tube and a CO + CO₂ exhaust tube on the cathode side, and an

O₂ outlet tube on the anode side. The whole system can be heated to the operating temperature of 800-1000 °C. Experiments can be performed to investigate the overall oxygen production capabilities of a particular electrolyte/electrode combination. Based on these test results conclusions can be drawn as to the effectiveness of particular cells.

CONCLUDING REMARKS AND SUMMARY

To date we have developed an understanding of the processes involved in electrolytic separation of oxygen from carbon dioxide, and are currently in a position to begin investigating materials that may afford increases in ion conductivity that will result in increased cell performance.

An effective technique has been established for the fabrication of cells, and we have demonstrated the ability to manufacture working cells. A test-bed has been built to conduct experiments, which are currently under way.

Future work will include investigation of electrolytes other than the fluorite structures, and oxide or perovskite electrodes. Also, some of the other fabrication techniques such as tape casting will be investigated. In addition, electrode application techniques will be considered in great detail. The overall oxygen plant design will be significantly simplified if the electrochemical cell operated efficiently at close to Martian atmospheric pressures. Hence, extensive tests will be performed to study the effect of sub atmospheric (< 1 bar) CO₂ supply pressures.

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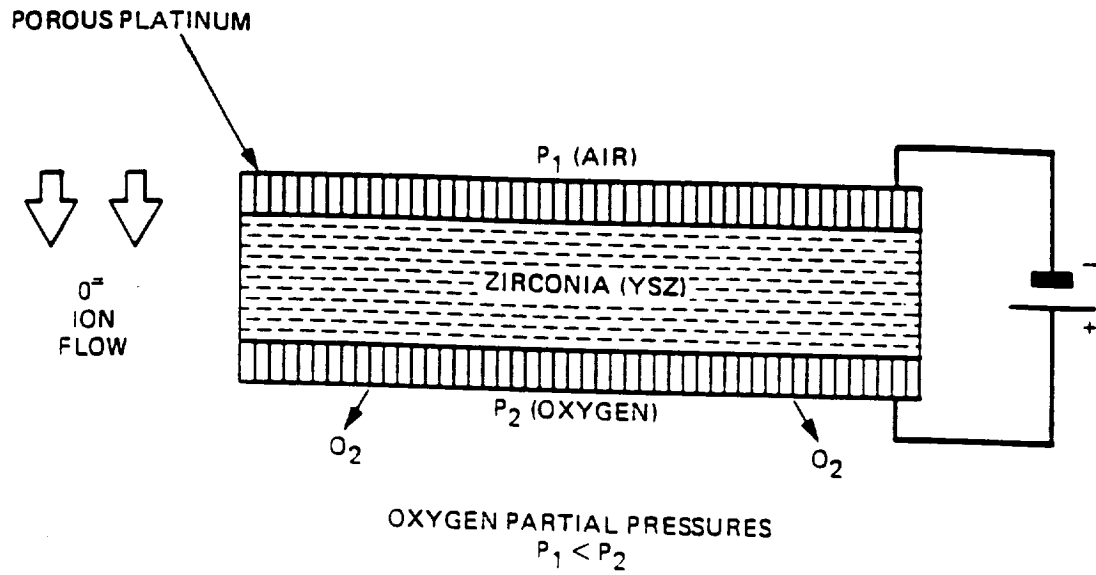


Fig 1: Schematic of an Electrochemical Separation Cell [6]

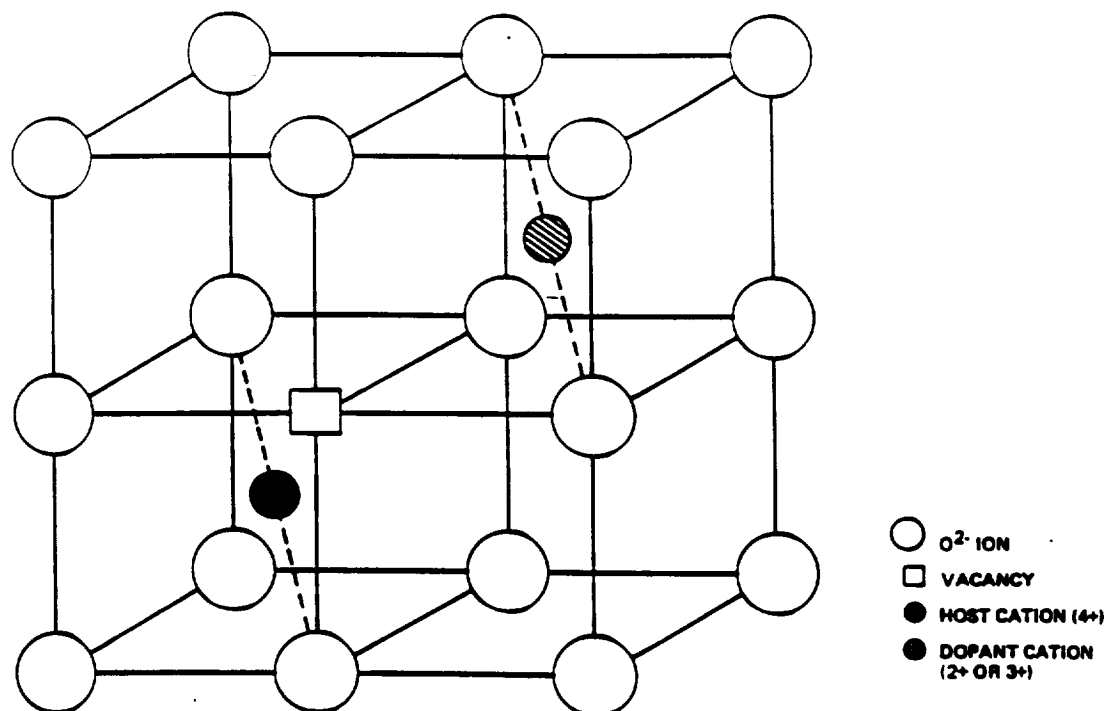


Fig 2: Distorted Fluorite Structure [6]

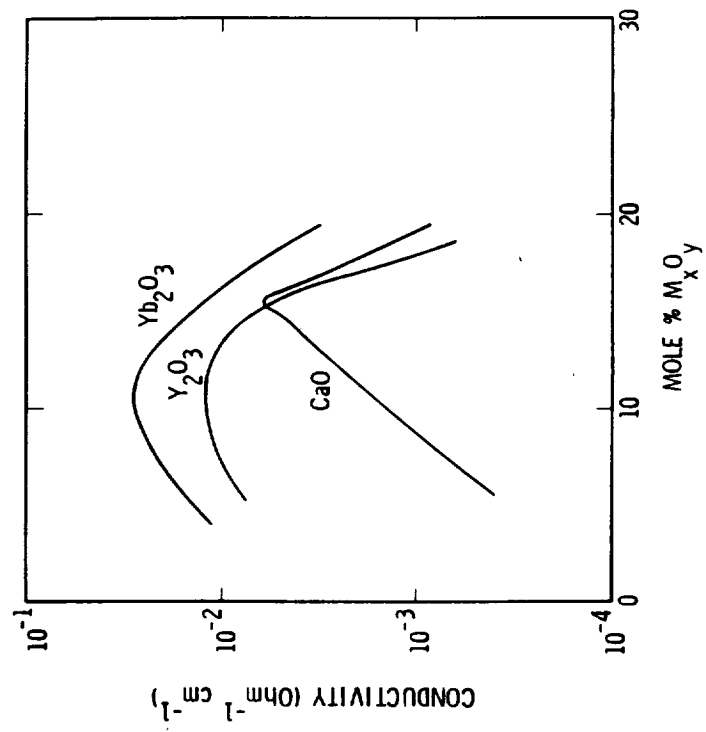


Fig 3: Dopant Concentration For Yttria Stabilized Zirconia [6]

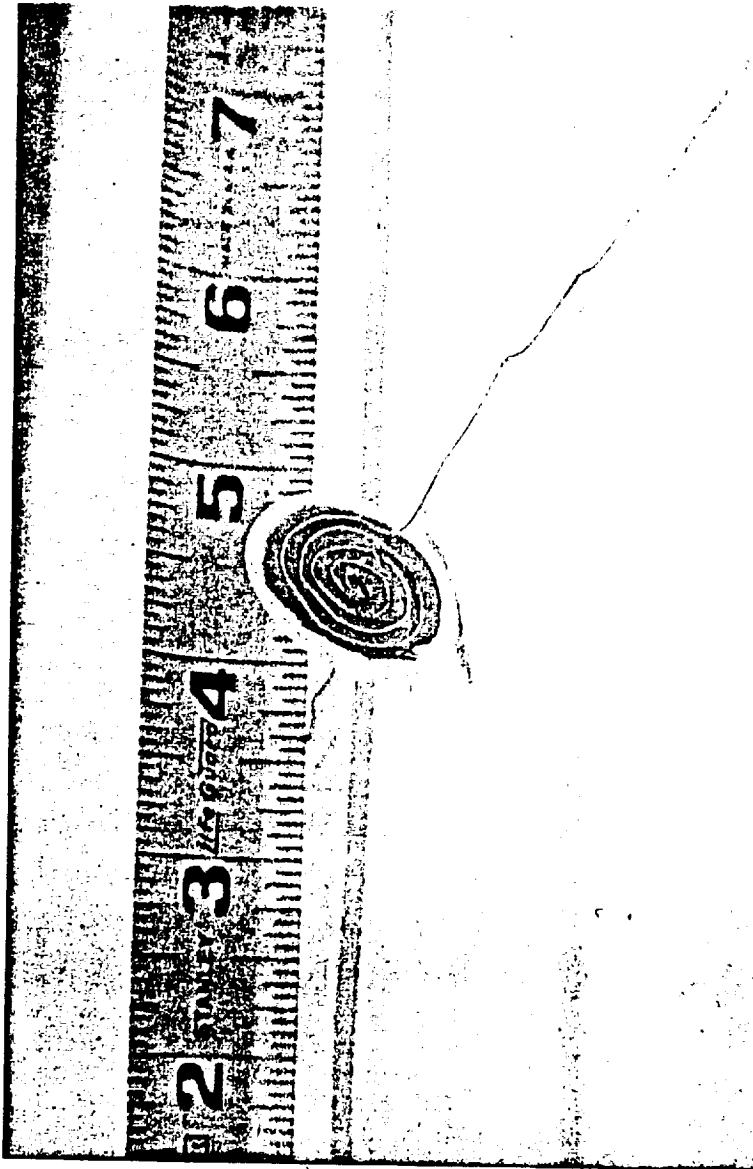


Fig 4: Electroded Electrochemical Disk With Lead Wires

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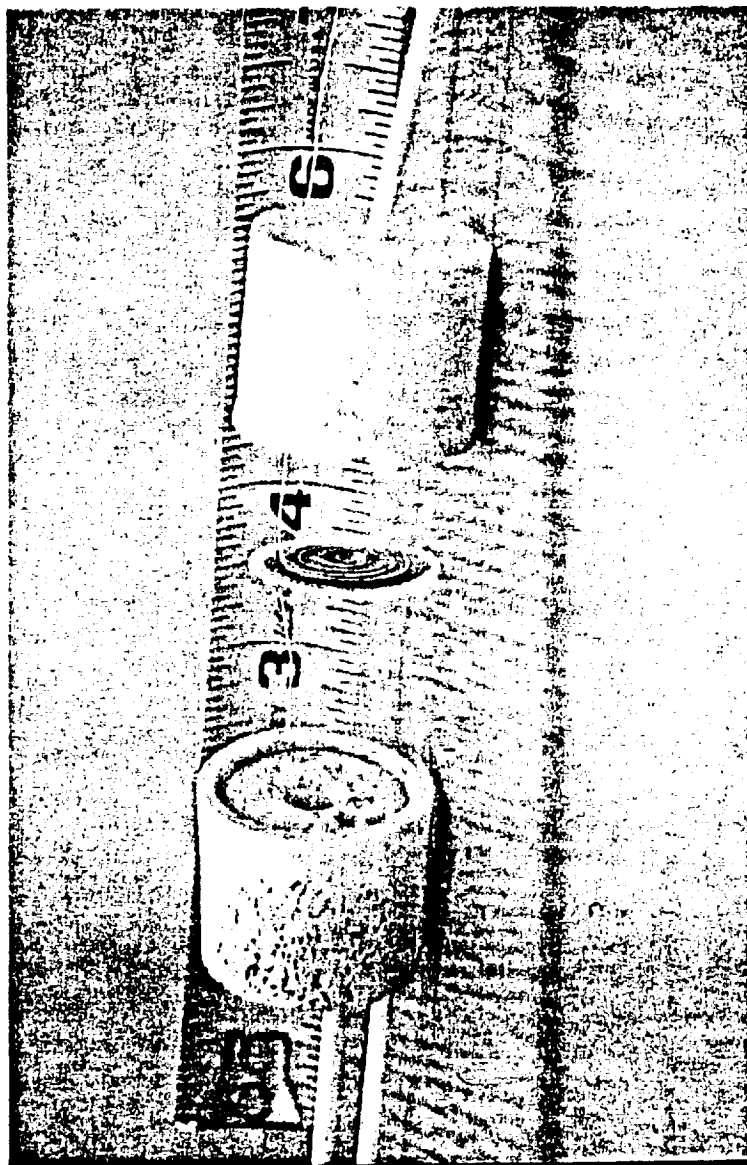


Fig 5a: Disk With Manifolds and Supply Wires Ready to be Assembled

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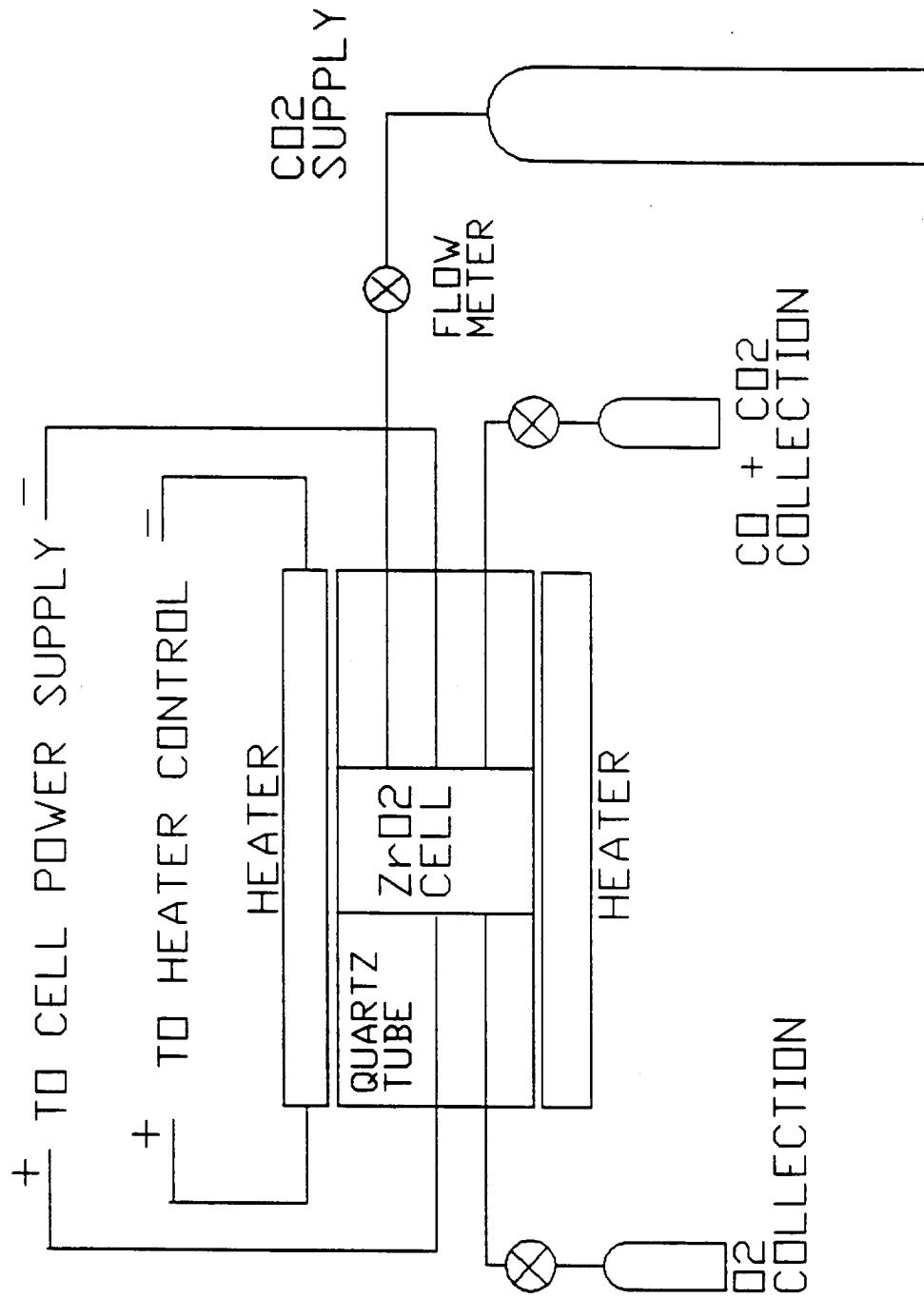


Fig 5b: Schematic of an Assembled Disk Module For Oxygen Production